UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF CHEMICAL SAFETY AND POLLUTION PREVENTION

MEMORANDUM

Date: May 15, 2012

SUBJECT: Pyrethrins/Piperonyl Butoxide: Air Concentration Following an Application of a Pyrethrum and Piperonyl Butoxide Product in a Mosquito Misting System under Static Conditions with a Nozzle Height of 6 Feet.

PC Code: 069001 / 067501
Decision No.:
Petition No.:
Risk Assessment Type: NA
TXR No.:
MRID No.: 48695801; 48695802

DP Barcode: D398003
Registration No.:
Regulatory Action:
Case No.:
CAS Nos.: PY 8003-34-7; PBO 51-03-6
40 CFR:

Ver.Apr.2010

FROM: Ivan D. Nieves, Chemist
Health Effects Division (HED) (7509P)/Risk Assessment Branch IV

THROUGH: Matt Lloyd, Industrial Hygienist
Health Effects Division (HED) (7509P)/Risk Assessment Branch VII

TO: Jose Gayoso, RM 52
Pesticide Re-Evaluation Division (7508P)

The study was reviewed according to the applicable sections of the OPPTS Series 875 Group B-Post Application Guidelines (Guidelines 875.2500- inhalation exposure). The study received a primary review from Versar and secondary review from HED. Based on the study review, the data are valid for use in human health risk assessments for pyrethrins and piperonyl butoxide to represent typical outdoor residential misting systems at the application rate that the study was conducted at. There are caveats to the appropriate use of this data in human health risk assessment that are outlined in the secondary review.

Table 1, below shows a summary of results for the two trials. The two trials had different sampling intervals, but in evaluating the data HED believes the two trials are appropriate to combine to compare. While the flow rates and sampling durations are not presented in the study report, HED estimated and presented the approximate residues in mg/m^3 using the information presented in the study report. Table 2 provides additional detail on the air concentration measurements.

Conclusions:

For the 5 foot height sampler the highest air concentrations (0.076 mg/m^3 for PY and 0.352 mg/m^3 for PBO) were recorded the first 15 minute period after Application #1. For the 2 foot height sampler the highest concentrations (0.101 mg/m^3 for PY and 0.656 mg/m^3 for PBO) were recorded during the first 15 minutes after Application #1. These concentrations are much lower than the expected concentrations of 0.48 mg/m^3 for PY and 2.4 mg/m^3 for PBO based on the application rate. The first 3 samples were summed for the two heights to represent a 0-60 minute air concentration. The air concentration at the two heights for the summed samples were virtually identical. The five foot height had calculated air concentrations of 0.05 mg/m^3 for pyrethrins and 0.21 mg/m^3 for piperonyl butoxide.

The difference between the two applications is that two more set of samples was collected after Application #1 and the first three sampling intervals were shorter. Comparing the available information indicates that there is not a significant difference between the 2 release heights of the nozzles. After 60 minutes, only a fraction of the initial air concentration remains airborne.

While the study is appropriate for use in human health risk assessment to represent postapplication air concentrations for pyrethrins and piperonyl butoxide from use of typical mosquito misting systems, there are limitations with the study data (outlined in the "limitations" section below). Because of these limitations, HED believes the data set is appropriate to use for the application rate the study was conducted at but not the higher application rate available for use on the product label.

Limitations:

The study was reviewed according to the applicable sections of the OPPTS Series 875 Group B-Post Application Guidelines (Guidelines 875.2500- inhalation exposure). The following issues were identified:

- The study report did not provide details of sample handling or storage for the field fortification samples or the field samples. Field fortification samples did indicate that the PY I and PBO residue levels were stable but the analysis dates for field fortification samples and field samples were not provided. Subsequent communication with the registrant identified that the samples were stored frozen and analyzed within 30 days of the sampling.
- Details such as actual flow rate and actual sampling duration times were not provided in the study report. The residue levels were reported only as µg/sample. The results in mg/m^3 presented in this review were estimated assuming a flow rate of 1 liter per minute and duration times presented in the study report.

- The study report made no mention of breakthrough or retention studies.
- The potential product application rate for this product is 2x as high as monitored in this study.
- Method validation results and analytical parameters were not provided with the study report.
- There was only one fortification sample per fortification level for each sampler height.
- The Registrant did not correct the raw residue data for field fortification recoveries.

Utility of this Data Set for Chemical Generalizability:

At this time, HED does not believe this data set is appropriate to generalize to other chemicals beyond pyrethrins and piperonyl butoxide. HED reviewed two iterations of this study protocol in 2009 (D366720/D370782) and included a number of recommendations and the guideline checklist to ensure all aspects of the study conduct were appropriate for use in human health risk assessment. This study fell short of the protocol reviews in a number of ways that limits the utility of this data set beyond pyrethrins and piperonyl butoxide. The absence of this study information introduces significant uncertainty into the interpretation and utility of this data set beyond a limited range. The major points that limit the utility of this data for generalizability include:

- The study was not conducted at the maximum application rate. While study data conducted for other application rates are useful, HED believes it is most appropriate to conduct a study at the maximum application rate.
- The study guidelines for 875.2500 clearly state that "Retention and breakthrough studies should be performed under conditions similar to those anticipated in the field phase of the study to ensure that collected material is not lost from the medium during sampling. It is recommended that at least one test be carried out where the initial trap contains 10x the highest amount of residue expected in the field." While the registrant indicated in subsequent emails that previous work was completed to this end at some unspecified time in the past, HED did not review this data for the original air concentration study conducted at the two ft. height (D346411; MRID 47062801) or with this data set.
- The study guidelines clearly state that "residues should be reported as ug/sample and airborne concentration." The study report provided limited information on actual sampling flow rates and sampling times that would allow for the data to be presented in this way. While the registrant indicated in subsequent emails that some work was completed to this end, the study report insufficiently addressed this issue.
- The 2012 Residential SOPs contain a screening level assessment for post-application inhalation exposure to mosquito misting systems that include an integrated air concentration for an estimated 2.3 hour exposure duration per day. This study provides useful data for a single "pulse" of insecticide. However, HED believes that the actual use pattern may include post-application inhalation exposure to multiple "pulses" of an insecticide.

Below, Table 1 outlines air concentration calculations for pyrethrins and piperonyl butoxide for multiple time points in the study.

Table 1: Air Concentration Calculations for Pyrethrins and Piperonyl Butoxide

Location	Sample ID	Interval (minutes)	Calculated Air Concentrations (mg/m3)			
			Trial 1		Trial 2	
			Total PY	Corrected PBO	Total PY	Corrected PBO
2 foot	Sum of 3 samples	0 to 60	0.04	0.24	0.04	0.21
5 foot	Sum of 3 samples	0 to 60	0.04	0.18	0.05	0.21
2 foot	AT-T1-L1-2-60	60 to 120	0.01	0.03	0.01	0.04
5 foot	AT-T1-L2-5-60	60 to 120	0.01	0.03	0.01	0.05
2 foot	AT-T1-L1-2-120	120 to 180	0.00	0.01	0.00	0.01
5 foot	AT-T1-L2-5-120	120 to 180	0.001	0.008	0.003	0.01
2 foot	AT-T1-L1-2-180	180 to 240	0.0005	0.003	0.001	0.005
5 foot	AT-T1-L2-5-180	180 to 240	0.001	0.003	0.001	0.01

- The results for residue in mg/m^3 are estimates based on a 1 Lpm flow rate and sample duration presented in the study report. Actual flow rates and duration times were not provided in the study report.

Table 2: . PY and PBO Air Concentration Following Mosquito Mister Application to a Test Chamber

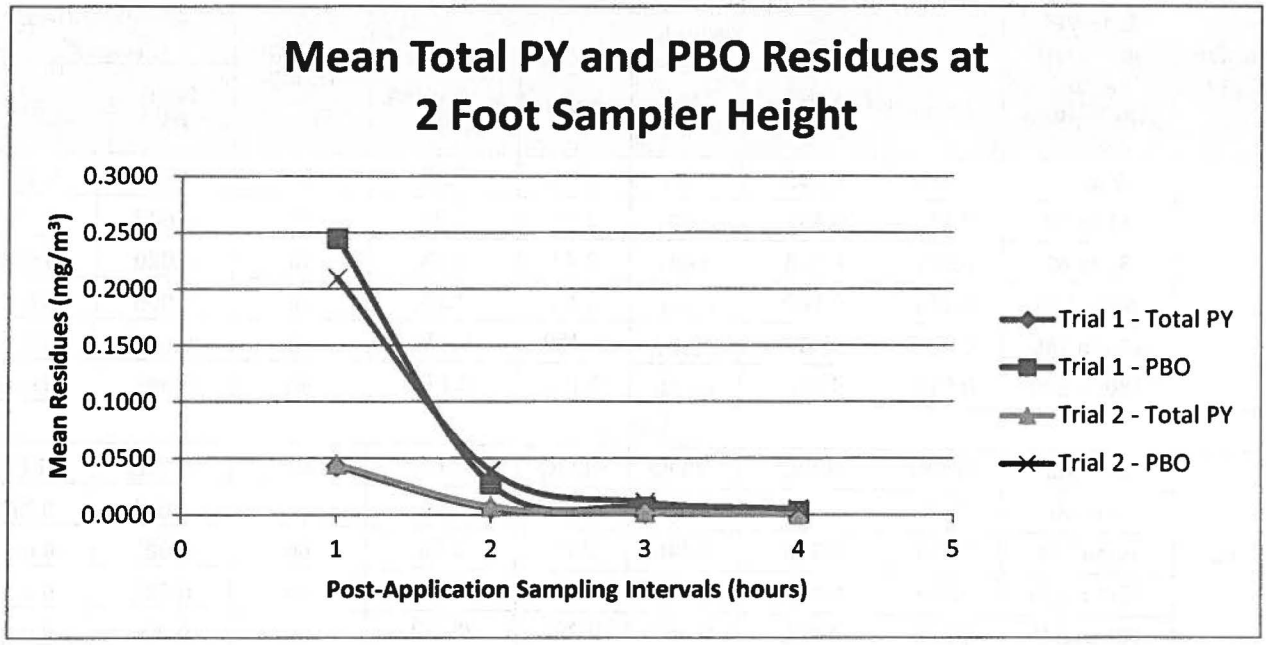
Sampler Height	Interval (minutes) after Application	Air Concentration (µg/tube)					Duration (min)	Estimate of Air Concentration[b] (mg/m^3)	
		PY I	Corrected PY I	Total PY[a]	PBO	Corrected PBO		Total PY	PBO
Trial 1									
2 foot	Pre-app	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	60	<LOQ	<LOQ
	0 to 15	0.704	0.805	1.52	8.61	9.84	15	0.101	0.656
	15 to 30	0.242	0.276	0.522	2.07	2.37	15	0.035	0.158
	30 to 60	0.244	0.278	0.526	2.16	2.47	30	0.018	0.082
	60 to 120	0.148	0.169	0.319	1.44	1.65	60	0.005	0.027
	120 to 180	0.042	0.042	0.078	0.418	0.410	60	0.001	0.007
	180 to 240	0.015	0.015	0.027	0.162	0.159	60	0.0005	0.003
5 foot	Pre-app	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	60	<LOQ	<LOQ

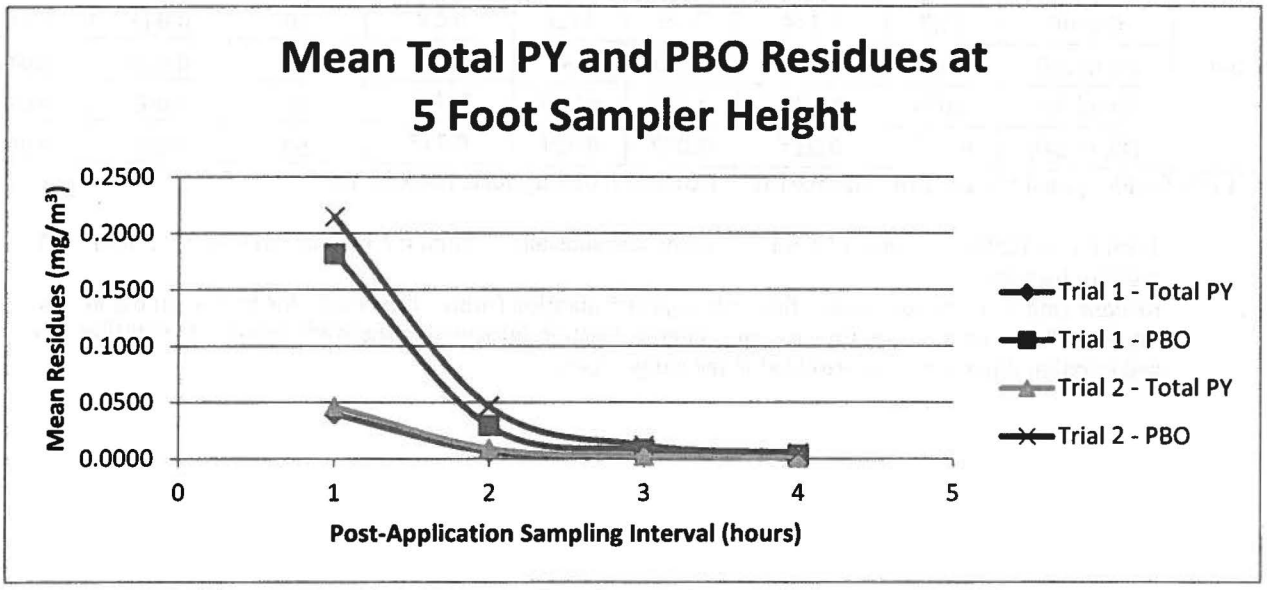
Table 2: . PY and PBO Air Concentration Following Mosquito Mister Application to a Test Chamber									
Sampler Height	Interval (minutes) after Application	Air Concentration (µg/tube)					Duration (min)	Estimate of Air Concentration[b] (mg/m^3)	
		PY I	Corrected PY I	Total PY[a]	PBO	Corrected PBO		Total PY	PBO
	0 to 15	0.531	0.605	1.14	4.62	5.28	15	0.076	0.352
	15 to 30	0.291	0.332	0.627	2.50	2.86	15	0.042	0.190
	30 to 60	0.279	0.318	0.601	2.43	2.78	30	0.020	0.093
	60 to 120	0.166	0.189	0.358	1.54	1.76	60	0.006	0.029
	120 to 180	0.047	0.047	0.087	0.489	0.479	60	0.001	0.008
	180 to 240	0.016	0.016	0.030	0.175	0.172	60	0.001	0.003
Trial 2									
2 foot	Pre-app	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	60	<LOQ	<LOQ
	0 to 60	1.24	1.42	2.68	11.0	12.6	60	0.045	0.210
	60 to 120	0.207	0.236	0.446	2.04	2.33	60	0.007	0.039
	120 to 180	0.065	0.074	0.139	0.674	0.661	60	0.002	0.011
	180 to 240	0.025	0.025	0.047	0.298	0.292	60	0.001	0.005
5 foot	Pre-app	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	60	<LOQ	<LOQ
	0 to 60	1.29	1.474	2.79	11.3	12.9	60	0.046	0.215
	60 to 120	0.252	0.287	0.543	2.45	2.80	60	0.009	0.047
	120 to 180	0.073	0.083	0.158	0.738	0.724	60	0.003	0.012
	180 to 240	0.027	0.027	0.049	0.321	0.315	60	0.001	0.005

LOQ for PY I, total PY and PBO was 0.0108, 0.020, and 0.020 µg/tube, respectively.

a Total PY is 52.9% PY I and 47.1% PY II in the test substance. Total PY residue (µg/tube) = (1.89) * PY I residue (µg/tube)

b Residue (mg/m^3) = residue (µg) / flow rate (Lpm) * duration (min). The results for residue in mg/m^3 are estimates based on a 1 Lpm flow rate and sample duration presented in the study report. Actual flow rates and duration times were not provided in the study report.


Mean Total PY and PBO Residues at 2 Foot Sampler Height
Mean Residues (mg/m³)
0.3000
0.2500
0.2000
0.1500
0.1000
0.0500
0.0000
0
1
2
3
4
5
Post-Application Sampling Intervals (hours)
Trial 1 - Total PY
Trial 1 - PBO
Trial 2 - Total PY
Trial 2 - PBO


Mean Total PY and PBO Residues at 5 Foot Sampler Height
Mean Residues (mg/m³)
0.2500
0.2000
0.1500
0.1000
0.0500
0.0000
0
1
2
3
4
5
Post-Application Sampling Interval (hours)
Trial 1 - Total PY
Trial 1 - PBO
Trial 2 - Total PY
Trial 2 - PBO

EPA Reviewer: _____ **Signature:** _____
Health Effects Division (7509C) **Date:** _____

Template version 02/06

DATA EVALUATION RECORD

STUDY TYPE: Air Sampling Following Mosquito Mister Application to a Test Chamber: OPPTS Series 875.2500

TEST MATERIAL: Test substance is a 0.8511% dilution of PYROCIDE® Fogging Concentrate 7446 (Riptide®), EPA Registration Number 1021-1785 which is a water-based ultralow volume (ULV) concentrate formulation containing 5.0% pyrethrins and 25.0% piperonyl butoxide as the active ingredients.

SYNONYMS: Pyrethrum (PY); mixture of pyrethrin I (PY I) and pyrethrin II (PY II); CAS # 8003-34-7
Piperonyl butoxide (PBO): 2-(2-butoxyethoxy)ethyl 6-propylpiperonyl ether; Piperonylbutoxide; 3,4-Methylenedioxy-6-Propylbenzyl-n-Butyldiethyleneglycolether; 5-{[2-(2-butoxyethoxy)ethoxy]methyl}-6-propyl-1,3-benzodioxole; 2,2'-oxydiethanol - 5-(butoxymethyl)-6-propyl-1,3-benzodioxole (1:1); CAS # 51-03-6.

CITATION:

Authors:	John T. Bergmann and Janice K. Sharp, Ph.D.
Title:	Air Concentration Following an Application of a Pyrethrum and Piperonyl Butoxide Product in a Mosquito Misting System under Static Conditions with a Nozzle Height of 6 Feet
Report Date:	March 14, 2011
Field Site:	McLaughlin Gormley King Company (MGK) 8810 Tenth Avenue North Minneapolis, MN 55427
Analytical Laboratory:	Golden Pacific Laboratories (GPL) 4720 West Jennifer Ave. Suite 105 Fresno, CA 93722
Identifying Codes:	MGK Study # GLP-2242; GPL Study No. 090317; MRID 48695801; Unpublished

SPONSOR: Non-Dietary Exposure Task Force (NDETF)

EXECUTIVE SUMMARY:

This report reviews a study titled "*Air Concentration Following an Application of a Pyrethrum and Piperonyl Butoxide Product in a Mosquito Misting System under Static Conditions with a Nozzle Height of 6 Feet*" submitted by the Non-Dietary Exposure Task Force. The purpose of the study was to determine the concentration of pyrethrins (PY) and piperonyl butoxide (PBO) in the air following one 59 second application of diluted PYROCIDE® Fogging Concentrate 7446 (Riptide®). The application was made through a mosquito misting system under static conditions in an environmental chamber. This report is the second study conducted by MGK looking at air concentration following PY and PBO application in a mosquito misting system. The first study, MRID 47062801, was conducted with delivery air nozzles placed 2 feet above the ground in an environmental testing chamber. In this study, the delivery nozzles were placed at a height of 6 feet above the ground to simulate systems where nozzles are placed on fences or walls. The test product was diluted at 1.16 fluid ounces per gallon of deionized water to achieve a 0.046% PY and 0.23% PBO solution. Air concentration of PY and PBO was determined over a period of 4 hours after one application. The air monitoring samplers were placed at the height of two and five feet above the floor to simulate an adult and toddler entering such an area immediately after application. The test substance was applied using a CoastalMister Mosquito Mister connected to six Hago #4023 anti-drip nozzles positioned along the perimeter of the walls. The mister nozzles were placed 6 feet above the floor at a 45 degree downward facing angle. The system operated at 146 pounds per square inch (psi). An average of 174.6 grams (total of all six nozzles) of test substance was sprayed per 60 second application and one application was made at the beginning of each of the two test runs. A particle size analysis was performed prior to the first application (Trial #1) and following the second application (Trial #2).

The same environmental test chamber was used for both test trials in the study. The indoor environmental test chamber was 5,848.5 ft^3 (166 m^3) in size. Two test runs were conducted and the investigators ventilated the chamber between runs. The chamber was not ventilated during the test runs until after the air sampling was completed. The spray contained 0.046% PY and 0.23% PBO and the chamber volume was 166 m^3, therefore the application rate was 0.48 mg/m^3 for PY and 2.4 mg/m^3 for PBO.

Two OVS, XAD-2 air sampling tubes were attached to air pumps in the center of the room at 2 and 5 feet above the floor. The air pumps were set at a flow rate of 1.0 liters/minute (Lpm). For Trial #1, one air sample was collected at 0, 15, 30, 60, 120, and 180 minutes after the application for both heights. For Trial #2, one air sample was collected at 0, 60, 120, and 180 minutes after the application for both heights. The OVS tubes were extracted using acetonitrile and a platform shaker and the analysis was performed using HPLC with mass spectrometry. The limit of quantification was 0.02 µg/sample for both PY and PBO. Prior to each application, a control and three field fortification samples were generated. One OVS tube was spiked for each of three fortification levels and sent with the field samples to the laboratory for analysis. The overall average field recovery was 92.3% for PY with a range of 80 of 107% and the average field recovery was 92.3% for PBO with a range of 78.5 to 109%. All of the PY and PBO results from the air sampling intervals were corrected for corresponding field fortification recoveries. The air samples collected for 60 minutes prior to each application had no detectable residues above the LOQ.

For air monitoring samplers at the five foot height, the highest concentration for total PY was 0.076 mg/m^3. The highest concentration for PBO was 0.352 mg/m^3. These levels were recorded at the first 15 minute sampling interval after the first application (Trial #1).

For samplers at the two foot height, the highest concentration for total PY was 0.101 mg/m^3. The highest concentration for PBO was 0.656 mg/m^3. These levels were recorded at the first 15 minute sampling interval after the first application (Trial #1).

The study was reviewed according to the applicable sections of the OPPTS Series 875 Group B- Post Application Guidelines (Guidelines 875.2500- inhalation exposure). The following issues were identified:

- The study report did not provide details of sample handling or storage for the field fortification samples or the field samples. Field fortification samples did indicate that the PY I and PBO residue levels were stable but the analysis dates for field fortification samples and field samples were not provided.
- Details such as actual flow rate and actual sampling duration times were not provided in the study report. The residue levels were reported only as µg/sample. The results in mg/m^3 presented in this review were estimated assuming a flow rate of 1 liter per minute and duration times presented in the study report.
- The study report made no mention of breakthrough or retention studies.
- Method validation results and analytical parameters were not provided with the study report.
- There was only one fortification sample per fortification level for each sampler height.
- The Registrant did not correct the raw residue data for field fortification recoveries.

COMPLIANCE: Signed and dated GLP, Quality Assurance, and Data Confidentiality statements were provided. The study sponsor waived claims of confidentiality within the scope of FIFRA Section 10 (d) (1) (A), (B), or (C). The Study Report indicated that the study was conducted under EPA Good Laboratory Practice Standards (40 CFR Part 160), with the following exception: in the Protocol, there was an error in the fortification levels of the spiked tubes. The report reflects the raw data obtained during the study. This error did not have any impact on the validity of the study.

CONCURRENT EXPOSURE STUDY? No

GUIDELINE OR PROTOCOL FOLLOWED:
This study was conducted according to the McLaughlin Gormley King Company (MGK) study protocol No. 2242 and OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Post-application Exposure Monitoring Test Guidelines, 875.2500, Inhalation Exposure. A compliance checklist is provided in Appendix A.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Material:

Formulation: PYROCIDE® Fogging Concentrate 7446 (Riptide®) is a water-based ultralow volume (ULV) concentrate formulation containing 5.0% pyrethrins and 25.0% piperonyl butoxide as the active ingredients. The test material was a 0.8511% dilution of the fogging concentrate resulting in a solution containing 0,046% PY and 0.23% PBO.

Lot/Batch # technical: Pyrethrin: AA8729
Piperonyl butoxide: 20788
Deuterated ($^2H_4$)-Piperonyl Butoxoide Internal Standard: IN-AN-B-100
Lot/Batch # formulation: Not reported.
Purity: Pyrethrin standard: 19.48% total (exp. Date7/22/09)
Piperonyl butoxide standard: 96.0% (exp. date 10/24/09)
CAS #(s): Pyrethrin: 8003-34-7
Piperonyl Butoxide: 51-03-6

Other Relevant Information: EPA Registration No. 1021-1785

2. Relevance of Test Material to Proposed Formulation(s):
The test product label was provided with the Study Report. The label specifies a dilution of 1.16 ounce of product per gallon of system tank size (or one half gallon of product added to 54.5 gallons of water to fill a 55 gallon tank) for use in Automatic ULV spraying systems. This yields a PY concentration of 0.046%, and a PBO concentration of 0.23% in the spray solution.

B. STUDY DESIGN
The study protocol was provided in the study report. There was one protocol amendment and one protocol deviation. The protocol amendment addressed changes to the proposed experimental start and stop dates, reference substance identification information, and procedure for preparing the field fortification standards. The protocol deviation stated that the field fortification levels in the tubes from the study were different than indicated in the protocol. The protocol was in error; therefore, this deviation did not negatively impact the integrity of the results presented in this study.

1. Site Description:

Test locations: The study was conducted in an environmental test chamber located at McLaughlin Gormley King Company in Minneapolis, MN. Two consecutive test trials took place in the same environmental test chamber.

Meteorological Data: The temperature and humidity was measured inside the test chamber and recorded throughout the trial using a data logger. The exhaust fans were turned off during the application. After the last air sample was collected for each trial, the chamber was vented by turning on the exhaust fans. On the day of the first trial, temperatures ranged from 72.1 to 74.5°C with an average temperature of 73.3°C. The relative humidity ranged from 18.3 to 24.1% with an average relative humidity of 19.8%. On the day of the second trial, temperatures ranged from 71.3 to 73.8°C with an average temperature of 72.9°C. The relative humidity ranged from 15.1 to 18.3% with an average relative humidity of 16.6%.

2. Site Monitored:

Room(s) Monitored: One environmental test chamber was used in the study. The walls of the test chamber were covered with a plastic sheet and the floor was covered with on layer of Kraft paper.

Room Size(s): 27 ft x 25 ft 9 inches x 11 feet 6 inch ceiling, or 5,848.5 ft^3 (166 m^3)

Other products used: N/A

3. **Physical State of Formulation as Applied:** Mist spray

4. **Application Rates and Regimes:**

Application Equipment: A CoastalMister TM System, Digital 2 Mosquito Mister was used to apply the test product. The mister was connected to six Hago type #4023 anti-drip nozzles positioned near the walls at a 45 degree downward angle They were situated 6 feet above the floor.

Application Regime: The system was operated at 146 psi. Two trials were conducted with the misting system operating for 59 seconds each. The chamber was ventilated after the last sampling interval for each trial.

Application rate(s): The test product was diluted at 1.16 fluid ounces per gallon of deionized water to achieve a 0.046% PY and 0.23% PBO solution. One application was made at the beginning of each test run. The spray contained 0.046% PY and 0.23% PBO and the chamber volume was 166 m^3, therefore, the application rate was 0.48 mg/m^3 for PY and 2.4 mg/m^3 for PBO. The application rate used in the study was the label recommended application rate. This is considered to be a typical use rate. The label also includes a 2X higher rate (i.e., 0.093% PY and 0.46% PBO) that is recommended for high populations of insects or hard to control species.

Prior to the first misting application, a sample of the diluted test product was retained for verification. The label recommended nozzle coverage area was 100 square feet per nozzle. The actual nozzle coverage was not reported.

Equipment Calibration Procedures: The application system was calibrated by placing containers of known weight over the nozzles, operating the system for a 60 second spray and reweighing the containers. An average of 174.6 grams (sum of all six nozzles) of test substance (X-6282-07) was sprayed per 60 second application.

Was total deposition measured? Total deposition was not measured.

5. **Exposure Monitoring Methodology**:

Method and Equipment: Air concentration was monitored using two MSA Escort ELF air sampling pumps attached to SKC OVS sampling tubes (226-30-16). These tubes contain a 13 mm glass fiber filter followed by two sections of XAD-2 sorbent.

Sampling Procedure: The pumps operated at 1.0 liter per minute for 15 to 60 minutes per sample. Air concentration was monitored for 4 hours following application. One air sampling tube each was positioned open end down, centered in the room at two feet above the floor to represent a toddlers breathing zone, and five feet above the floor to represent an adult breathing zone. The details of sample handling and shipping were not discussed in the report.

The analytical report from the laboratory was not included in the study

report, therefore, the exact dates of analysis are not known. Given that the study was initiated on January 4, 2010 and final report was completed on March 14, 2010, it can be assumed that the samples were analyzed within two months of collection.

Replicates per activity:

– Replicates per sampling time: At each sampling interval, one sample was collected at each sampler height.

– Number of sampling intervals: There were a total of seven sampling intervals for OVS tubes for Trial #1 and five sampling intervals for Trial #2. Both include one pre-application interval.

Times of sampling: For Trial #l, one air sample was collected at each height at prior to the application and at 0, 15, 30, 60, 120, and 180 minutes after the application. For Trial #2, one air sample was collected at each height prior to the application and at 0, 60, 120, and 180 minutes after the application

6. **Sample Handling:**

Two trials were conducted using the same environmental test chamber. The analytical report from the laboratory was not included in the study report, therefore, the exact dates of analysis are not known. Pre-treatment calibrations occurred on January 15, 2010 and January 26, 2010. Given that the study was initiated on January 4, 2010 and final report was completed on March 14, 2010, it can be assumed that the samples were analyzed within two months of collection. According to the study protocol, each tube was placed in a plastic bag and stored in a freezer until transfer to the analytical laboratory for analysis. No information on storage temperature or storage location is provided.

7. **Analytical Methodology:**

Extraction method: The contents of the air sampling tube were extracted with 7 ml of acetonitrile using a platform shaker for 15 minutes. Samples having higher residue levels were diluted to an appropriate final volume using 50% acetonitrile: 50% water.

Detection Method(s): The HPLC/MS/MS operating conditions were not provided with the report.

Method Validation: The samples were analyzed using method GPL-MTH-070 which was developed and validated by Golden Pacific Laboratories for the analysis of PY I and PBO by HPLC/MS/MS. The validation took place prior to study initiation; however, method validation results were not reported. The method LOQ for both PY and PBO was 0.02 µg/sample.

Instrument Performance and Calibration: The HPLC/MS/MS responses (peak areas) were determined for a series of calibration standards. The concentrations of the standards (and IS for PBO) injected and their corresponding peak responses were used to calculate a standard calibration curve using linear regression and a correlation coefficient (r) based on the standard (and IS for PBO) concentrations and their respective peak responses or peak response ratio for PBO.

Quantification: The total amount of pyrethrins in the sample was quantified as the sum of the measured residues of pyrethrin I (PY I) plus the calculated residues of pyrethrin II (PY II). The amount of PY II residues were estimated based upon the amount of pyrethrins in the reference test substance (52.9% PY II, 47.1% PY I). The

piperonyl butoxide residues were quantified as piperonyl butoxide.

8. Quality Control:

Lab Recovery: A summary of the concurrent recovery results is provided in Table 1. All recoveries were within the acceptable range of 70% to 120%. One control sample was also run with the set of samples. PYI recoveries ranged from 93.6% to 99.1% with an overall average of 96.8% ± 2.16% (n=8). PBO recoveries ranged from 93.8% to 98.1% with an overall average of 96.3% ± 1.64% (n=8).

Table 1. Summary of Concurrent Fortification Recoveries

Matrix	Target Analyte	Fortification Level (µg/sample)	N	Range of % Recoveries	Average % Recovery	Overall Average % Recovery	Std. Dev.
OVS Tubes	PYI	0.011	4	93.6 to 99.1	97.5	96.8	2.16
		1.11	4	93.7 to 97.3	96.2		
	PBO	0.021	4	93.8 to 97.1	95.3	96.3	1.64
		20.8	4	95.7 to 98.1	97.2		

Notes: LOQ for PYI and PBO is 0.02 µg/sample for air sampling tubes.

Field Blanks: Prior to each application, the test chamber was sampled for 1 hour at a flow rate of 1 liter per minute. There were no PY or PBO residues detected above the LOQ in the field blank samples.

Field Recovery: Field fortification samples were generated immediately prior to the conduct of each trial. The OVS tubes were spiked at one of three levels and sent with the field samples to Golden Pacific Laboratories for analysis. All of the recoveries were within the acceptable range of 70% to 120%. PYI recoveries ranged from 80.0% to 107% with an overall average of 92.3% ± 9.73% (n=6). PBO recoveries ranged from 78.5% to 109% with an overall average of 92.3% ± 10.3% (n=6).A summary of the field fortification results is provided in Table 2.

Table 2. Summary of Field Fortification Recoveries

Matrix	Target Analyte	Fortification Level (µg/sample)	N	Range of % Recoveries	Average % Recovery	Overall Average % Recovery	Std. Dev.
OVS Tubes	PYI	0.0108	2	96.3 to 107	102	92.3	9.73
		0.108	2	80.0 to 95.4	87.7		
		1.08	2	84.2 to 90.7	87.5		
	PBO	0.20	2	94.5 to 109	102	92.3	10.3
		2.0	2	78.5 to 96.5	87.5		
		20	2	85.0 to 90.5	87.8		

Breakthrough: The study report did not mention performing a breakthrough study.

Formulation: PYROCIDE® Fogging Concentrate 7446 (Riptide®) is a water-based ultralow volume (ULV) concentrate formulation containing 5.0% pyrethrins and 25.0% piperonyl butoxide as the active ingredients. The test material was a 0.8511% dilution of the fogging concentrate resulting in a solution containing 0,046% PY and 0.23% PBO.

Tank mix: Not applicable. The test substance was not applied with any other pesticides or adjuvants.

Travel Recovery: Travel recovery samples were not used for this study.

Storage Stability: Storage stability tests were not conducted. Field fortification sample recoveries were acceptable, however, no details as to whether they were stored or shipped or analyzed with the field samples was presented in the study report.

II. RESULTS AND CALCULATIONS:

The Registrant provided the total PY and PBO residues only as uncorrected µg/tube. Versar corrected all PY I and PBO results for corresponding average field fortification level recoveries. Figures 1 and 2 provide graphical representations of the mean residues (µg/tube) for each analyte at each sampling height. The Registrant did not provide actual sample flow rates and sampling durations. Versar calculated total PY and PBO residues as mg/m^3 based on the assumption that all samples were collected at a flow rate of 1 liter per minute at each of the proposed sample interval durations. Air sampling results are presented in Table 3 as µg/tube and mg/m^3.

For air monitoring samplers at the five foot height, the highest concentration for total PY was 0.076 mg/m^3. The highest concentration for PBO was 0.352 mg/m^3. These levels were recorded at the first 15 minute sampling interval after the first application (Trial #1).

For samplers at the two foot height, the highest concentration for total PY was 0.101 mg/m^3. The highest concentration for PBO was 0.656 mg/m^3. These levels were recorded at the first 15 minute sampling interval after the first application (Trial #1).

III DISCUSSION

A. LIMITATIONS OF THE STUDY:

The study was reviewed according to the applicable sections of the OPPTS Series 875 Group B- Post Application Guidelines (Guidelines 875.2500- inhalation exposure). The following issues were identified:

- The study report did not provide details of sample handling or storage for the field fortification samples or the field samples. Field fortification samples did indicate that the PY I and PBO residue levels were stable but the analysis dates for field fortification samples and field samples were not provided.

- Details such as actual flow rate and actual sampling duration times were not provided in the study report. The residue levels were reported only as µg/sample. The results in mg/m^3 presented in this

review were estimated assuming a flow rate of 1 liter per minute and duration times presented in the study report. .

- The study report made no mention of breakthrough or retention studies.
- Method validation results and analytical parameters were not provided with the study report.
- There was only one fortification sample per fortification level for each sampler height.
- The Registrant did not correct the raw residue data for field fortification recoveries.

B. CONCLUSIONS:

The study represents a worst case exposure scenario because it was conducted indoors with no ventilation and low humidity.

For the 5 foot height sampler the highest air concentrations (0.076 mg/m^3 for PY and 0.352 mg/m^3 for PBO) were recorded the first 15 minute period after Application #1. For the 2 foot height sampler the highest concentrations (0.101 mg/m^3 for PY and 0.656 mg/m^3 for PBO) were recorded during the first 15 minutes after Application #1. These concentrations are much lower than the expected concentrations of 0.48 mg/m^3 for PY and 2.4 mg/m^3 for PBO based on the application rate.

The difference between the two applications is that two more set of samples was collected after Application #1 and the first three sampling intervals were shorter. The chamber was not ventilated during the study author states that the decline in air concentration is due entirely to particle settling onto the walls and floor of the chamber.

Table 3. PY and PBO Air Concentration Following Mosquito Mister Application to a Test Chamber

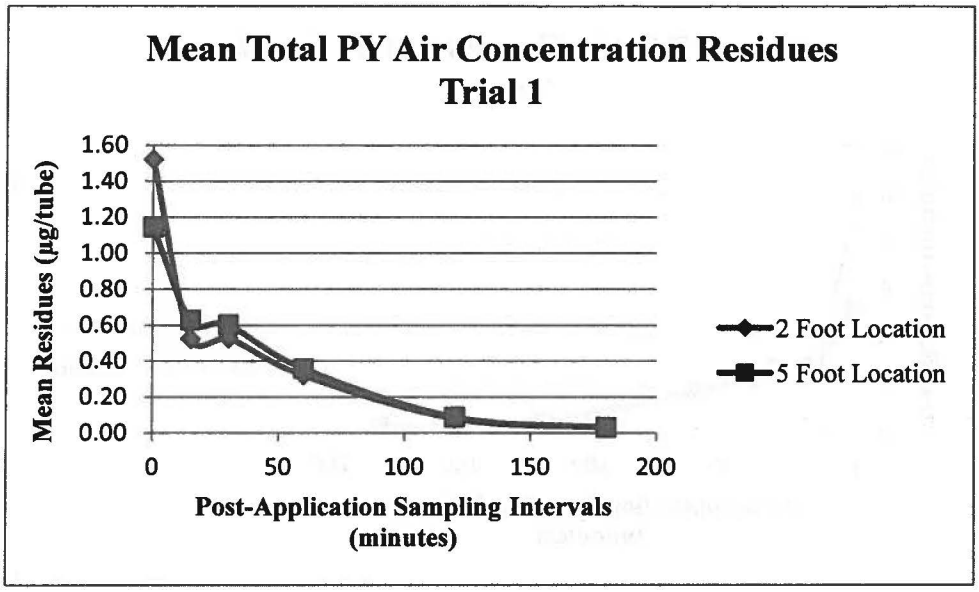
Sampler Height	Interval (minutes) after Application	Air Concentration (µg/tube)					Duration (min)	Estimate of Air Concentration[b] (mg/m^3)	
		PY I	Corrected PY I	Total PY[a]	PBO	Corrected PBO		Total PY	PBO
Trial 1									
2 foot	Pre-app	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	60	<LOQ	<LOQ
	0 to 15	0.704	0.805	1.52	8.61	9.84	15	0.101	0.656
	15 to 30	0.242	0.276	0.522	2.07	2.37	15	0.035	0.158
	30 to 60	0.244	0.278	0.526	2.16	2.47	30	0.018	0.082
	60 to 120	0.148	0.169	0.319	1.44	1.65	60	0.005	0.027
	120 to 180	0.042	0.042	0.078	0.418	0.410	60	0.001	0.007
	180 to 240	0.015	0.015	0.027	0.162	0.159	60	0.0005	0.003
5 foot	Pre-app	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	60	<LOQ	<LOQ
	0 to 15	0.531	0.605	1.14	4.62	5.28	15	0.076	0.352
	15 to 30	0.291	0.332	0.627	2.50	2.86	15	0.042	0.190
	30 to 60	0.279	0.318	0.601	2.43	2.78	30	0.020	0.093
	60 to 120	0.166	0.189	0.358	1.54	1.76	60	0.006	0.029
	120 to 180	0.047	0.047	0.087	0.489	0.479	60	0.001	0.008
	180 to 240	0.016	0.016	0.030	0.175	0.172	60	0.001	0.003
Trial 2									
2 foot	Pre-app	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	60	<LOQ	<LOQ
	0 to 60	1.24	1.42	2.68	11.0	12.6	60	0.045	0.210
	60 to 120	0.207	0.236	0.446	2.04	2.33	60	0.007	0.039
	120 to 180	0.065	0.074	0.139	0.674	0.661	60	0.002	0.011
	180 to 240	0.025	0.025	0.047	0.298	0.292	60	0.001	0.005
5 foot	Pre-app	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	60	<LOQ	<LOQ
	0 to 60	1.29	1.474	2.79	11.3	12.9	60	0.046	0.215
	60 to 120	0.252	0.287	0.543	2.45	2.80	60	0.009	0.047
	120 to 180	0.073	0.083	0.158	0.738	0.724	60	0.003	0.012
	180 to 240	0.027	0.027	0.049	0.321	0.315	60	0.001	0.005

LOQ for PY I, total PY and PBO was 0.0108, 0.020, and 0.020 µg/tube, respectively.

a Total PY is 52.9% PY I and 47.1% PY II in the test substance. Total PY residue (µg/tube) = (1.89) * PY I residue (µg/tube)

b Residue (mg/m^3) = residue (µg) / flow rate (Lpm) * duration (min). The results for residue in mg/m^3 are estimates based on a 1 Lpm flow rate and sample duration presented in the study report. Actual flow rates and duration times were not provided in the study report.

Figure 1. Mean Total PY Air Concentration Residues



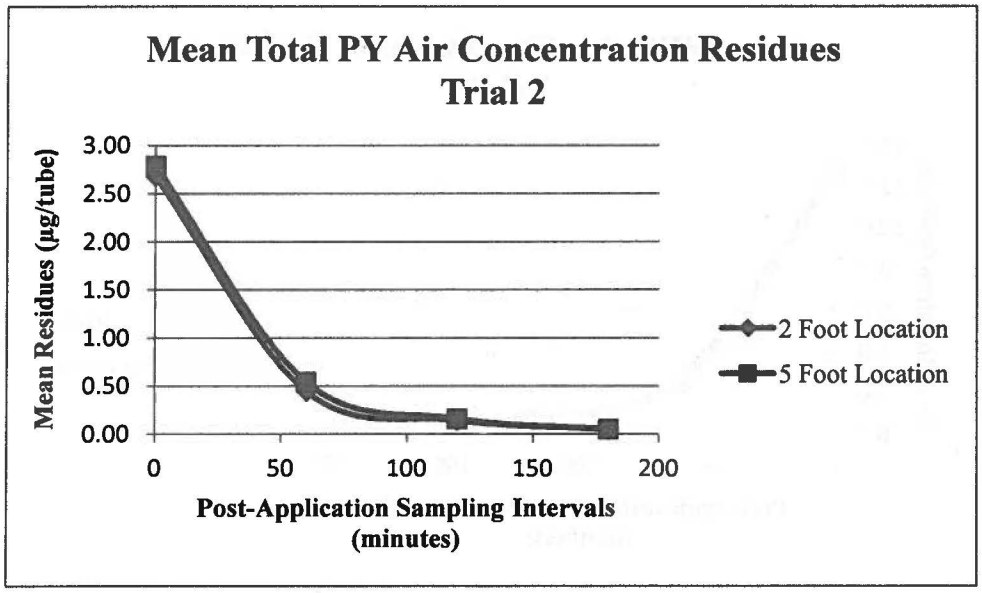
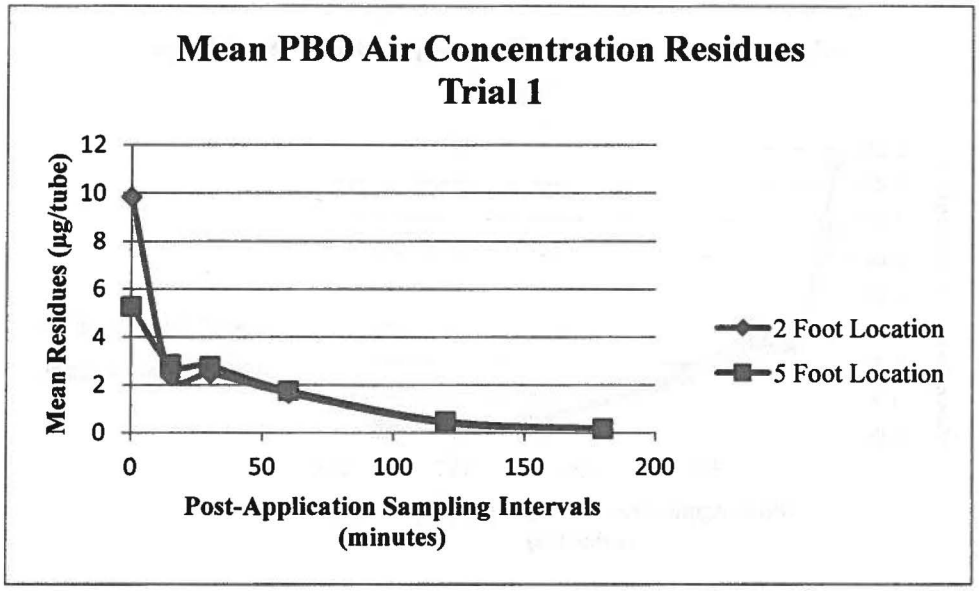
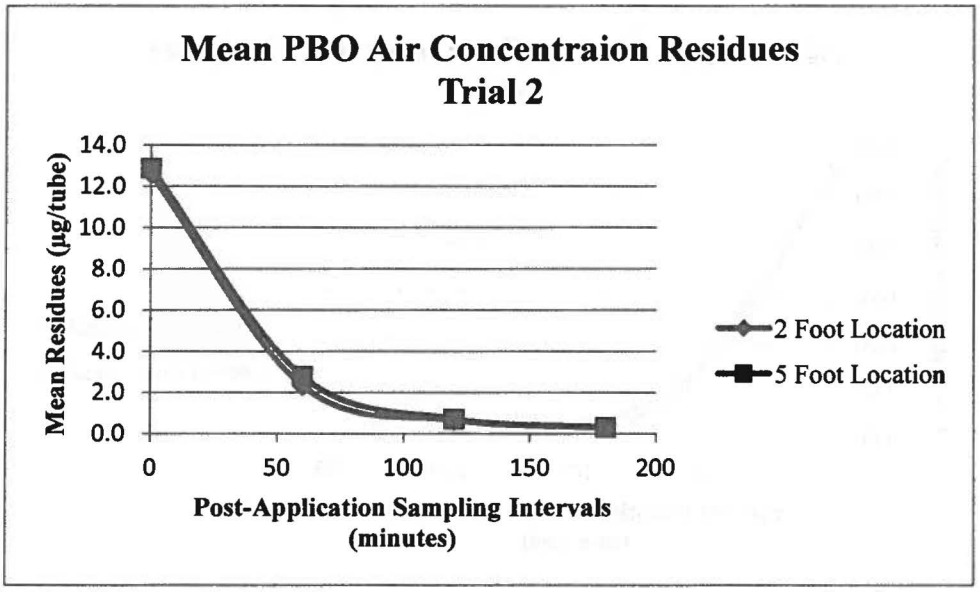


Figure 2. Mean PBO Air Concentration Residues





Name:
Evaluator
Occupational Exposure Assessment Section

Date

Name:
Peer Reviewer
Occupational Exposure Assessment Section

Date

Name:
Head,
Occupational Exposure Assessment Section

Date

Compliance Checklist for " Air Concentration Following an Application of a Pyrethrum and Piperonyl Butoxide Product in a Mosquito Misting System under Static Conditions with a Nozzle Height of 6 Feet "

GUIDELINE 875.2500 INHALATION EXPOSURE

- *The test substance must be the typical end use product of the active ingredient. This criterion was met.*

- *The production of metabolites, breakdown products, or the presence of contaminants of potential toxicologic concern, should be considered on a case-by-case basis.* This criterion was met. Metabolites PY I and PY II were considered in this study.

- *Applications should occur at the time of season that the end-use product is normally applied to achieve intended pest control.* This criterion was not applicable because the test product was applied indoors under static conditions.

- *The end use product should be applied by the application method recommended for the crop. Information that verifies that the application equipment (e.g., sprayer) was properly calibrated should be included.* These criteria were met.

- *The application rate used in the study should be provided and should be the maximum rate specified on the label. However, monitoring following application at a typical application rate is more appropriate in certain cases.* This criterion was not met. The label also includes a 2X higher rate (i.e. 0.093% pyrethrins, 0.46% PBO) that is recommended for high populations of insects or hard to control species.

- *If multiple applications are made, the minimum allowable interval between applications should be used.* This criterion is not applicable. Only one application was made.

- *A sufficient number of replicates should be generated to address the exposure issues associated with each population of interest. In general, the study should include a minimum of 15 replicates per activity, distributed as follows: 5 replicates (i.e., individuals) on each of 3 monitoring periods (i.e., days after application).* This criterion was not met. Only two monitoring trials were sampled, with one sample collected at the 2 foot and one at the 5 foot level during each trial.

- *The monitoring period should be of sufficient duration to result in reasonable detectability on dosimeters. Monitoring should be conducted before residues have dissipated beyond the limit of quantification. Baseline samples should be collected before the exposure activity commences.* These criteria were met.

- *The selected sites and seasonal timing of monitoring must be appropriate to the activity.* This criterion was met.

- *Studies should be conducted under different geographic/climatologic sites.* This criterion was not met. Both trials were conducted in an environmental testing chamber kept at the same humidity and temperature.*Inhalation monitoring techniques area (i.e., stationary) and/or personal monitoring) should contain sufficient samples to characterize the likely range of possible exposure concentrations, and to ensure that the reentry scenario can be adequately addressed.* This criterion was partially met. Stationary air monitoring took place at 4 to 6 intervals; however, only one sample was collected at each interval for each of two sampler heights.

- *Particulate levels should be monitored along with vapor phase concentrations unless adequate justification for not doing so is provided.* It is not certain if this criterion was met using OVS-XAD2 collection tubes.

- *Retention and breakthrough studies should be performed under conditions similar to those anticipated in the field phase of the study.* This criterion was not met. There was no mention of breakthrough or retention studies.

- *The sampling technique used should be appropriate, given the expected exposure scenario (e.g., the use of personal sampling pumps and sampling times consisting of filter cassettes and resin tubes or polyurethane foam filters is preferred; where personal sampling is not appropriate, stationary monitoring may be conducted.) Stationary samples should be collected from the center of treated fields and from at least 4 other locations, preferably at the cardinal compost points from the center location. Indoor sampling strategies should be designed based on the nature of the exposure scenario and building type. Samples should be collected at heights representing the breathing zones of the exposed populations (e.g., 18 inches for children; 48 inches for adults).* These criteria were met.

- *The duration of the sampling interval and air flow rates should be maximized within the appropriate flow rate range to increase the potential for capturing enough residue to be quantifiable.* This criterion was met.

- *Air flow rates should be recorded at the initiation and termination of the monitoring period, with the average being used in all calculations.* This criterion was met.

- *Samples should be stored in a manner that will minimize deterioration and loss of analytes between collection and analyses. Information of storage stability should be provided.* These criteria were not met. The study did not provide any information on the storage or handling of the samples. Field fortification samples did indicate that the PY I and PBO residue levels were stable but the analysis dates for field fortification samples and field samples were not provided.

- *Validated analytical methods of sufficient sensitivity are needed. Information on method efficiency (residue recovery) and limit of quantification (LOQ) should be provided.* These criteria were partially met. Method validation results were not provided with the report. The LOQs for PY I, Total PY, and PBO were provided.

- *Information on recovery samples must be included in the study report. A complete set of field recoveries should consist of at least one blank control sample and three or more each of a low-level and high-level fortification. These fortifications should be in the range of anticipated residue levels in the field study.* These criteria were partially met. There was only one fortification sample per fortification level for each height.

- *Raw residue data must be corrected if appropriate recovery values are less than 90 percent.* This

criterion was not met. The Registrant did not correct the raw residue data for field fortification recoveries.

- *Residues should be reported as µg pesticide active ingredient per sample and as an airborne concentration (µg/m^3). Distributional data should be reported, to the extent possible.* These criteria were partially met. The residues were reported as µg/sample only. The distributional data were reported.